

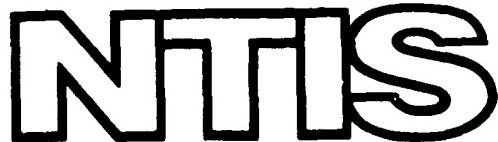
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ANTIOXIDANTS FOR USE IN COLOR PHOTOGRAPHIC DEVELOPERS

ARMY ELECTRONICS COMMAND

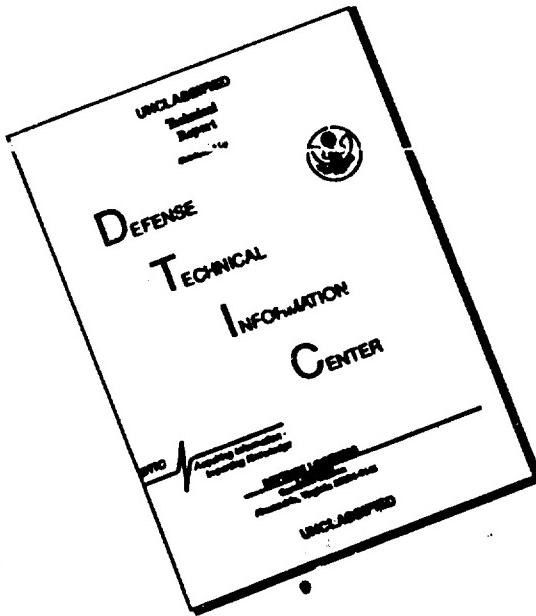
DECEMBER 1973

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The antioxidant properties were evaluated both during the processing stage and under storage conditions. Only a minimal improvement in developer stability during processing was noted. However, a significant improvement in developer stability during storage conditions was achieved.

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ANTIOXIDANTS FOR USE IN COLOR PHOTOGRAPHIC DEVELOPERS

by

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Photo Optics Technical Area
Combat Surveillance & Target Acquisition Laboratory

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1. INTRODUCTION

Exposed color film is usually developed in processing tanks containing the color photographic developer solution. During the processing steps, considerable aeration (oxidation) is produced by the passage of film through the developer solution, and by the exposure of the developer solution to atmospheric air. This type of aerial oxidation, if uncorrected by replenishing the developer with fresh solution, soon leads to serious loss in developer activity. Moreover, the problems of replenishing used color developer solutions are more complex than for conventional black and white processing. More complex chemical reactions occur during color development. The higher pH levels used in color developers render these developers more susceptible to aerial oxidation. There are more complex sensitometric requirements in color photographic processing. Finally, color photographic developer chemicals are usually more expensive than those used in black and white processing.

In order to minimize these difficulties, and to extend the useful life of color developer compositions, both in storage and during development, a systematic study of various antioxidants was undertaken. A total of 14 compounds was evaluated for antioxidant activity. Of these, two exhibited useful antioxidant properties. Di-hydroxy acetone¹, which has already been patented, and 2-anilinoethanol, on which an ECOM patent application has been filed, increases the storage stability of color developer compositions. In addition, it was found that 2-anilinoethanol functions, not only as an antioxidant, but also in greater concentration, as a development accelerator.

2. EXPERIMENTAL PROCEDURE

Three methods of screening and evaluating potential antioxidants were used. (1) A liter of color developer is prepared and divided into two 500 ml portions. One portion is kept as the control; to the other is added the antioxidant. Sensitometric exposures through a carbon continuous wedge are developed in each of the portions. Both portions are then placed in 500 ml beakers, uncovered, and with the liquid level marked. They are allowed to remain undisturbed for a period of 5 days. At the end of the 5-day period, the amount of liquid evaporated is replaced with water. An exposed wedge is then processed in each of the two solutions, and compared to the equivalent wedge prior to testing. (2) A more rigorous test of antioxidant effectiveness is to compare the activity of a developer protected with the antioxidant to the same developer unprotected, under conditions obtained in actual practice--that is, to develop enough film in a given quantity of developer so as to practically exhaust the developer, and then compare results between protected and unprotected developers. From the practical standpoint, antioxidant protection is more valuable during actual processing conditions than under static storage conditions. These tests are carried out as follows: just as in the previous illustration, one liter of

¹ U.S. Patent #3,615,503 (1971).

color developer is prepared and divided into two 500 ml portions. One portion is kept as control, the other has antioxidant added to it. Next, exposures through a continuous wedge, exactly as in the first illustration, are processed in each of the two solutions. Then 5 feet of completely exposed film of the same type and dimensions as those used in making the wedges, are processed in each developer in the usual manner. Next the degree of developer exhaustion is determined by again running exposed wedges through the two developer portions, and comparing the equivalent wedges prior to testing.

(3) An accelerated aging test accomplishes in several hours what might otherwise take several weeks. Just as in the previous examples, a liter of developer is divided into two 500 ml portions. One portion is kept as the control; to the other is added the antioxidant. Sensitometric strips are developed in these two developers. Next, each of the solutions is placed in a 500 ml Erlenmeyer flask which is connected to an aspirator pump. Room air is then bubbled through these solutions at a rate of about 2 liters a minute for a total time of 7 hours. Exposed wedges are again processed in the two solutions, and compared to the equivalent originals. Under these conditions of drastic air oxidation, the potential usefulness of an antioxidant is readily determined.

The accelerated aging test is also useful for determining the effective concentration range of antioxidant, in a reasonable time. By empirically varying the concentration of antioxidant and comparing the resultant sensitometric curves, the minimum effective concentration was found to be about 0.5%, with an upper limit of 1.0%, or less. At higher levels of antioxidant, developer activity is decreased. The only exception found was 2-anilinoethanol. In this case, the most effective concentration range was 0.10 - 0.15%. At 0.5 - 1.0%, the maximum used, developer activity was increased. At 1.0% concentration, however, antioxidant activity is only slightly better than at 0.10 - 0.15%.

In all cases, the film used was Eastman Kodak Ektacolor, Type S, Film 5026, 35mm. Sensitometric exposures were made in an Ansco Model 21 Intensity Scale Sensitometer using a 500-watt tungsten lamp, a daylight filter, and an M-type carbon wedge manufactured by Eastman Kodak. The voltage on the light source was adjusted so that a color temperature of 6500 Kelvin was obtained after passing through the wedge.

The exposed film was wound on Nikor reels and agitated with continual vertical agitation, each time lifting the reel clear of the developer and allowing 1 second of drainage, followed by 1 second immersion. This cycle was repeated for the total development time of 5½ minutes. The reel was next immersed in the bleach-fix for 3 minutes, followed by immersion in a water bath for 2 minutes. Processing temperature was maintained at 75°F ± 1°F.

Densities were measured on the Quantascan Automatic Densitometer, Model 11A. Transmission density was measured with three different filters having transmission values close to that specified in ASA Standard PH 2.1 - 1951. The wavelength at peak transmission for these filters were 440 nm for the blue, 530 nm for the green, and 630 nm for the red.

These three evaluative methods are illustrated in Figures 1, 2, and 3, for developers unprotected and protected by 2-anilinoethanol. Figure 1, a static stability test, illustrates the differences between a protected and unprotected developer. In curve 1c, unprotected, the blue and green lines have converged, and are no longer parallel, whereas in curve 1d, protected, the blue and green lines are still parallel, and are little different than either curve 1a, control, or 1b, the control plus the antioxidant.

Figure 2, which simulates actual processing conditions, illustrates the protective effect of a developer protected by 2-anilinoethanol compared to one unprotected, after developing the same quantity of film in each. As curve 2d shows, compared to curve 2c, only a minimal and insignificant improvement is achieved by the addition of the antioxidant.

Figure 3, illustrates an accelerated aging test, useful for quickly evaluating potential antioxidants. Curve 3c, unprotected, and curve 3d, protected by 2-anilinoethanol, illustrates this screening procedure. The protective effect of 2-anilinoethanol under conditions of drastic air oxidation is well illustrated.

3. DISCUSSION

a. General Principles

In the search for potential antioxidants, the basic assumption was made that oxidation (decomposition) of the color developer in storage, at least, proceeds by a free radical mechanism initiated by dissolved or atmospheric oxygen, and that the antioxidant functions as a radical terminator. With the exception of sulfite, few antioxidants have been employed in the photographic field. In the specific area of color photography, hydroxylamine and its derivatives are occasionally used.

The problem of oxidative stability, however, has long been recognized and rather thoroughly investigated in the field of polymer chemistry, rubber and petroleum technology, and food processing. In each of these areas, a free radical type of oxidation is the common denominator. It was hoped, therefore, that this fund of prior experience could be applied to the problem of extending the useful life of color developers.

To be a useful antioxidant in a photographic developer, the compound should not react adversely with other components in the developer and should not adversely affect the development potential. In addition, it should be sufficiently water soluble, and stable in solution. Toxicity is also an important factor. Within these limitations, the compounds listed were singled out for intensive evaluation

- (1) di methyl phosphite
- (2) fructose
- (3) mono-ethanolamine
- (4) di-phenyl carbazide
- (5) N-phenyl glycine

- (6) di-tertiary N-cresol
- (7) m-methoxy phenol
- (8) ammonium sulfamate
- (9) hydroxy phenyl glycine
- (10) 2-anilinoethanol
- (11) 1-phenyl semi carbazide
- (12) N,N'-aniline diacetic acid
- (13) di hydroxy acetone
- (14) acetyl glycine

In general, water soluble aromatic amines proved most successful. For example, the use of N-phenyl glycine, $C_6H_5NHCH_2COOH$, and hydroxy phenyl glycine, $HOC_6H_4NHCH_2COOH$, as antioxidants in color photographic developer compositions have been patented.² Both, however, have the undesirable property of decreasing the activity of the developer. A search was then made for related compounds without these drawbacks. 2-anilinoethanol, $C_6H_5NHCH_2CH_2OH$, structurally similar to the above, was found to function not only as an effective antioxidant, but also as a development accelerator. In concentrations of about 0.1 - 0.15%, 2-anilinoethanol was the most successful antioxidant investigated; by increasing the concentration to about 0.5 - 1.0%, it was possible to lower development time from the usual $5\frac{1}{2}$ to $4\frac{1}{2}$ minutes while still retaining essentially the same sensitometric characteristics.

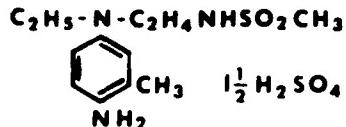
Another class of compounds, not related to aromatic amines has been used successfully. Di hydroxy acetone is the antioxidant of choice in this series of compounds. An evaluation of this compound, together with 2-anilinoethanol, forms the basis for this report.

b. General Chemistry of Processing

All color developing agents included in developer compositions in common use are derivatives of para-phenylene diamine. An example of a widely used color developing agent is the compound β -methanesulphanamidoethyl ethyl amino toluidine sesqui-sulfate, known in the trade as simply CD-3 or CD-3 color developing agent. This compound is made by Eastman Kodak.



PARA PHENYLENE
DIAMINE



CD3

² U.S. Patent #2,728,669

Although the antioxidants investigated will react in similar fashion with any para-phenylene diamine, CD-3 was used as the color developing agent in developer formulations. The color developer used is made up as follows:³

CD-3	7.5 grams
Na ₂ SO ₃	2.0 grams
benzyl alcohol	5.0 ml
NaOH	15.0 grams
borax	60.0 grams
K Br	1.5 grams
water to make	1000.0 ml

$$\text{pH} = 11.5$$

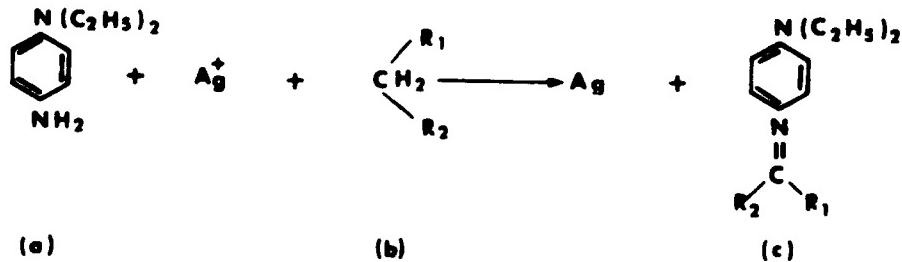
Another component of the processing system is a combined bleach-fixing bath, made up as follows:

ammonium thiosulfate	100.0 grams
iron salt of ethylene diamine tetracetic acid (EDTA)	100.0 grams
sodium sulfite	6.7 grams
water to make	1000.0 ml

$$\text{pH} = 5.8 - 6.0$$

In the initial step of development, the color developing agent, CD-3, reduces AgBr to metallic silver, and in the process is itself oxidized. Simultaneously, the developer is exposed to atmospheric oxygen during the agitation step of processing. Little can be done to alleviate the normal oxidation of the developer during the reduction step with silver bromide; however, an ideal antioxidant should retard the effects of atmospheric oxygen during processing. Unfortunately, no antioxidant investigated is capable of any more than a marginal and insignificant improvement in this respect. The primary usefulness of an antioxidant is simply to increase the keeping qualities of a developer under static storage conditions.

As mentioned previously, the initial reaction of the developer agent with exposed silver halide is reduction to metallic silver accompanied by oxidation of the developer:



³ Marilyn Levy and Harmon A. Willey, "A Rapid Color Negative Processing System," ECOM-4089, March 1973.

In the above equation, (a) is a para-phenylene diamine type color developer; (b) is a simplified formula for a color coupler; (c) is the final object of the photographic process, a colored dye molecule made up of color forming compounds in the emulsion and of developing agent added during processing. It is obvious that each time a dye molecule is formed, a corresponding amount of developer is consumed. This is the principal reason for developer exhaustion during processing.

Although not truly relevant to a discussion of oxidation, the reactions of the bleach-fix formula in the complete processing system is included for completeness. After formation of the colored dye image, it is necessary to remove the metallic silver from the emulsion. This is done by oxidizing metallic silver to Ag^+ , in which state it forms a soluble complex with ammonium thiosulfate. Ferric iron is commonly used for this purpose. However, ferric iron will also react with ammonium thiosulfate, since ammonium thiosulfate is a reducing agent. If this occurs, the desired oxidation of Ag to Ag^+ by ferric iron will not take place, or will go so slowly as to be useless. By forming a complex with EDTA, the redox potential of ferric iron is shifted so that the undesirable reaction with ammonium thiosulfate is prevented, while still permitting the oxidation of Ag to Ag^+ . Sodium sulfite is added as a preservative to prevent the rapid decomposition of ammonium thiosulfate.

c. Structure and Mechanism of Antioxidants

Whether by exposure to the atmosphere during processing or to dissolved air while stored as a liquid, the developer is degraded by another type of oxidation--direct combination with oxygen. In this case, the mechanism is more complex and still incompletely understood. Two possibilities exist, formation of a developer-free radical complex and formation of a developer-peroxide complex. When sustained by available oxygen, these reactions continue until the developer has been degraded into useless end products. It is with the inhibition of this type of oxidation reaction, that this report is concerned.

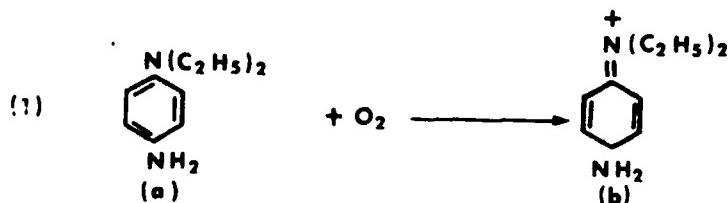
Antioxidants may be broadly grouped into two classes, those that inhibit oxidation through reactions with free radicals, and those that decompose peroxides into non-radical stable products. The free radical class of antioxidants is composed principally of secondary aromatic amines and substituted phenols; phosphites and various types of sulfur compounds form the principal type of peroxide decomposers. At the beginning of this investigation, it was not known which type of antioxidant would prove effective. Where possible, both types were evaluated, depending on water solubility and compatibility with the components of the developer.

It was found early in the investigation that phosphites, sulfur compounds, and substituted phenols were completely ineffective; emphasis was shifted to aromatic amines, with varying degrees of success. Secondary aromatic amines were most effective. N-phenyl glycine, hydroxy phenyl glycine, and 2-aminoethanol proved most successful. A brief investigation of the effect of structure, and of the position of the amine radical was also conducted.

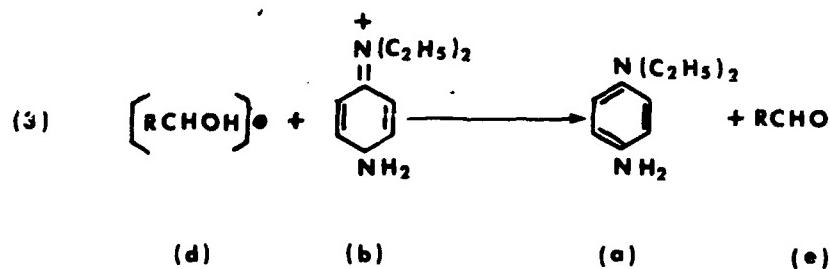
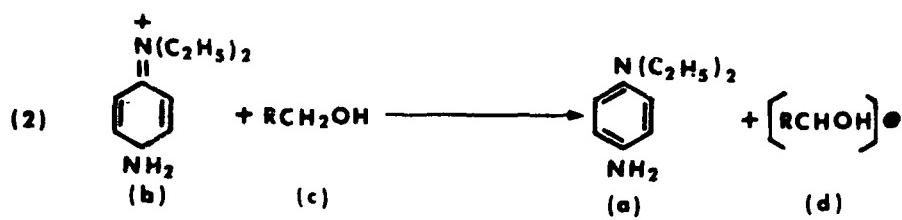
The three examples just given have the general structure $C_6H_5N'CH_2C\ldots$. A search was made of other amine compounds in which the amine was not necessarily a secondary amine or was not attached directly to a phenyl, or was not even aromatic. Carbanilide, $C_6H_5NHCONHCO_2H$, might be expected to be highly effective since it is composed of two C_6H_5NH radicals. This compound, however, was useless. N-carbobenzoxy glycine, $C_6H_5CH_2OCONHCH_2COOH$, was chosen since it contains an NH and a phenyl group and a 2 carbon group attached to an amine. However, the amine is not attached directly to the phenyl radical. This compound was also useless. Acetyl glycine, $CH_3CONHCH_2COOH$, was evaluated since it is a secondary amine containing a $CH_2C\ldots$ group attached to the amine, although not aromatic. Results were again negative. Finally, two compounds, both structurally similar to the successful antioxidants, but tertiary rather than secondary amines, were evaluated. The compounds were 2,2'-phenylimino-diethanol, $C_6H_5N(CH_2CH_2OH)_2$, and N,N'-aniline-diacetic acid, $C_6H_5N(CH_2COOH)_2$. No antioxidant activity was noted with either of the above compounds.

Almost all the antioxidants evaluated have been utilized in the polymer, rubber technology, or petroleum fields. In addition, the mode of oxidation of polymers, rubber, and petroleum products is similar to that of CD-3 developing agent--that is, free radical and/or peroxide formation. It was expected, therefore, that many of the antioxidants would be effective in the photographic field also. The fact that only three antioxidants, N-phenyl glycine, para hydroxy phenyl glycine, and 2-anilinoethanol, all secondary aromatic amines, were useful, is an interesting aspect of this study.

Di-hydroxy acetone is also an effective antioxidant. Because di-hydroxy acetone is structurally different from the other antioxidants tested, a brief study was made of its mode of action. Its formula $(CH_2OH)_2CO$, is that of a primary alcohol. Theory states⁴ that primary and secondary alcohols inhibit auto-oxidation because the initial free radical formed from them can transfer a second hydrogen atom and, thus become a stable aldehyde or ketone. In the process, the original free radical, formed in the oxidative process becomes stabilized and the oxidative process is inhibited. These reactions can be illustrated by the following equations:



⁴ Carl R. Noller, Chemistry of Organic Compounds, 2nd Edition, W. B. Saunders Company, page 887.



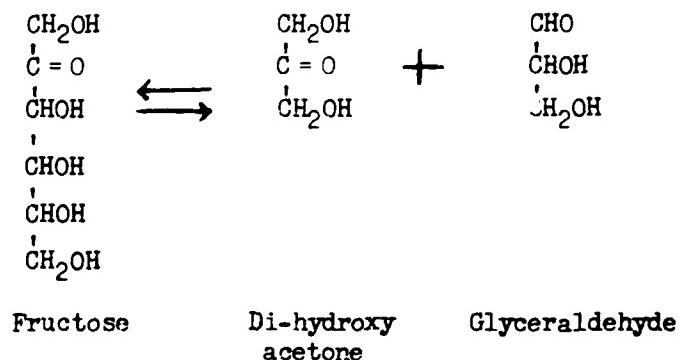
Equation (1) represents the initial oxidation of (a), para-phenylene diamine color developer to the semiquinone free radical state (b). Equation (2) illustrates the antioxidant mechanism of a primary alcohol (c), with the semiquinone (b). Here a hydrogen has been transferred from the primary alcohol group (c), to the semiquinone radical (b). In the process, the original para-phenylene diamine is reformed (a), and a secondary alcoholate free radical remains (d). Since this secondary alcoholate radical (d), is still capable of transferring another hydrogen, the hydrogen transfer process to the semiquinone (b), is repeated, again reforming the original para-phenylene diamine (a). When only a stable aldehyde RCHO (e), remains, the antioxidant activity is terminated.

Because the antioxidant activity of di-hydroxy acetone worked so effectively in practice, and was supported by a straight forward theoretical mechanism, a search was made for analogous alcohol types as possible antioxidants. Glycerol, $\text{CH}_2\text{OHCHOHCH}_2\text{OH}$, and ethylene glycol, $\text{CH}_2\text{OHCH}_2\text{OH}$, might, on the basis of the foregoing reactions, be expected to have useful antioxidant properties. Both these compounds were evaluated in concentrations from 0.10 to 1.0%; neither exhibited the slightest antioxidant activity with CD-3 color developer. It is interesting to note, however, that as far back as 1898, the use of alcohols as oxidation retardants for sodium sulfite was published.⁵

5 W. O. Lundberg, Autoxidation and Antioxidants, Interscience Publishers,
1962, page 478.

Fructose, $\text{CH}_2\text{OHCOCHOHCHOHCHOH}_2\text{OH}$, ordinary fruit sugar, is structurally similar to di-hydroxy acetone. The antioxidant properties of this compound were therefore evaluated, and with favorable results.

Fructose, in alkaline solution (such as exists in the developer) undergoes degradation to di-hydroxy acetone and glyceraldehyde, according to the following equations:⁶



Both di-hydroxy acetone and glyceraldehyde are claimed in the Kodak patent as antioxidants.⁷ This degradation in alkaline solution into the two compounds above, is quite possibly the basic reason for the antioxidant activity of fructose.

A cost comparison was made between fructose and di-hydroxy acetone; based on purchase costs, there is no price advantage in using fructose rather than di-hydroxy acetone.

As mentioned previously, 2-anilinoethanol can function as a development accelerator also, that is in concentrations up to about 1%, development time can be cut from $5\frac{1}{2}$ to about $4\frac{1}{2}$ minutes. One reason for this might be that aromatic amines are also weak reducing agents, hence may also be weak photographic developers. Only a brief time was spent on this.

Figure 4 illustrates the effects of a 1.0% concentration of 2-anilinoethanol on the sensitometric curves of the color developer. Curve 4a, the control, is the usual 5½ minute development; 4b is the control plus 1.0% 2-anilinoethanol, also a 5½ minute development. The increase in developer activity is interesting. Curve 4c also contains 1.0% antioxidant, but development has been cut to 4½ minutes. In curve 4d, also with 1.0% 2-anilinoethanol, development has been cut to 4 minutes. Fog level, relative speed point measured at 0.1 above fog, and gamma measured along the straight line portion of the curves, are as follows:

⁶ Carl R. Noller, Chemistry of Organic Compounds, 2nd Edition, W. B. Saunders Company, pages 368-69.

⁷ U.S. Patent #3,615,503 (1971) assigned to Eastman Kodak Company.

		<u>Fog</u>	<u>Speed Point</u>	<u>Gamma</u>
Curve 4a 5½ minutes	red	.20	.87	.63
	green	.76	.87	.80
	blue	.93	.73	.82
Curve 4b 5½ minutes	red	.26	.77	.85
	green	.82	.74	.98
	blue	1.00	.64	1.14
Curve 4c 1½ minutes	red	.20	.90	.62
	green	.78	.86	.85
	blue	.96	.82	.90
Curve 4d 4 minutes	red	.18	1.16	.55
	green	.72	1.00	.86
	blue	.92	.90	.83

Note the similarity in data between curves 4a, the control, and 4c, with the antioxidant, and a 4½ minute development.

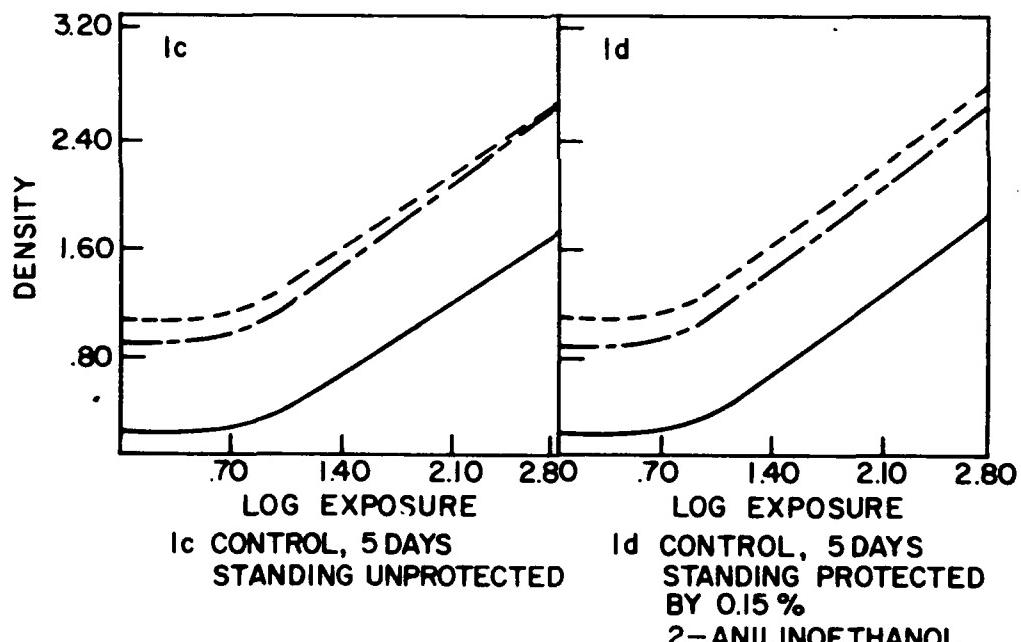
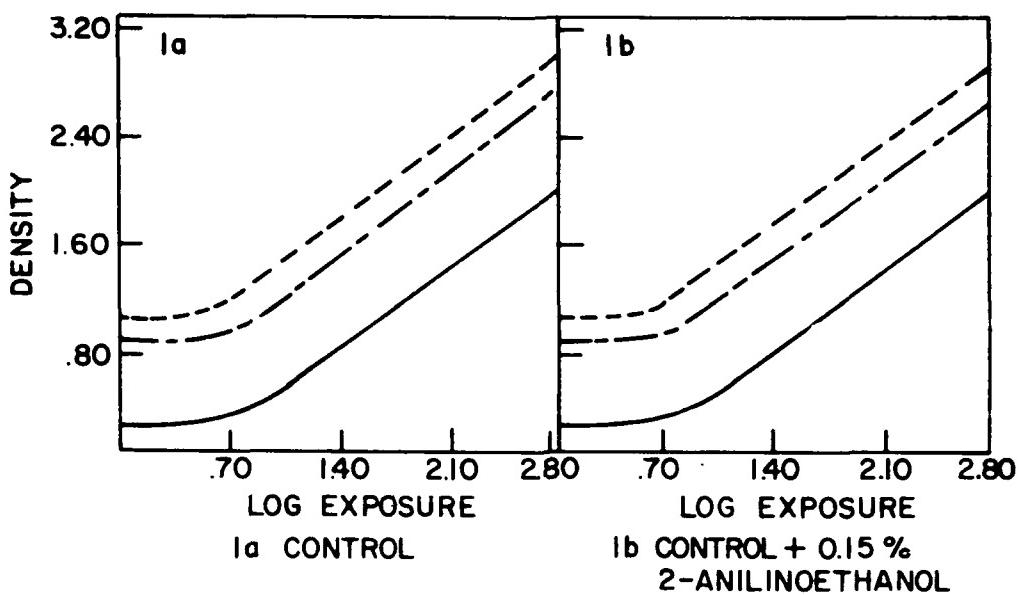
A static stability comparison test of the three antioxidants utilized in this investigation, together with a control, is illustrated in Figures 5, 6, 7, and 8. These tests were run concurrently. The pH values were taken of the developer alone, plus the antioxidant, and after each 5-day period. As is to be expected, the unprotected control shows the greatest pH loss; there is no significant differences in pH change among the three protected samples. The 5 and 10-day time period was chosen so as to show relative differences in antioxidant activity. The 10-day control, curve 5c, is obviously the worst. A comparison of fructose, di-hydroxy acetone, and 2-anilinoethanol, shows fructose to be the least effective, curve 6d. There is no appreciable difference between di-hydroxy acetone, curve 7d, and 2-anilinoethanol, curve 8d.

4. CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER STUDY

Few guidelines exist for the study of antioxidants in color photography. No thorough investigation has yet been undertaken in this area. Of all the antioxidants evaluated in this report, only 2-anilinoethanol and di-hydroxy acetone can be used without adversely affecting developer activity. No clear cut theory exists for the exact mechanism of antioxidant activity in the photographic field. The fact that certain primary alcohol groups and secondary aromatic amines, known as free radical inhibitors, are effective antioxidants, indicates that a free radical mechanism is the most probable type of oxidation of color photographic developers.

The role of 2-anilinoethanol as a development accelerator should be explored further. Unlike di-hydroxy acetone or N-phenyl glycine, a related compound, increasing its concentration in the developer also increases developer activity. In this connection also, the role of 2-anilinoethanol as an accelerator with hydroquinone type developers and in black and white processing in general, should be investigated.

Water soluble secondary aromatic amines and certain types of alcohol groups, adjacent to a carbonyl group, were most effective antioxidants. However, a thorough survey of this field has not yet been conducted. The influence of the chemical structure of the antioxidant on developer oxidation would be a productive field for more systematic study.



----- BLUE ----- GREEN ----- RED

Figure 1. Static Stability Test. Five-day exposure of developer to air, unprotected and protected by 0.15% 2-anilinoethanol.

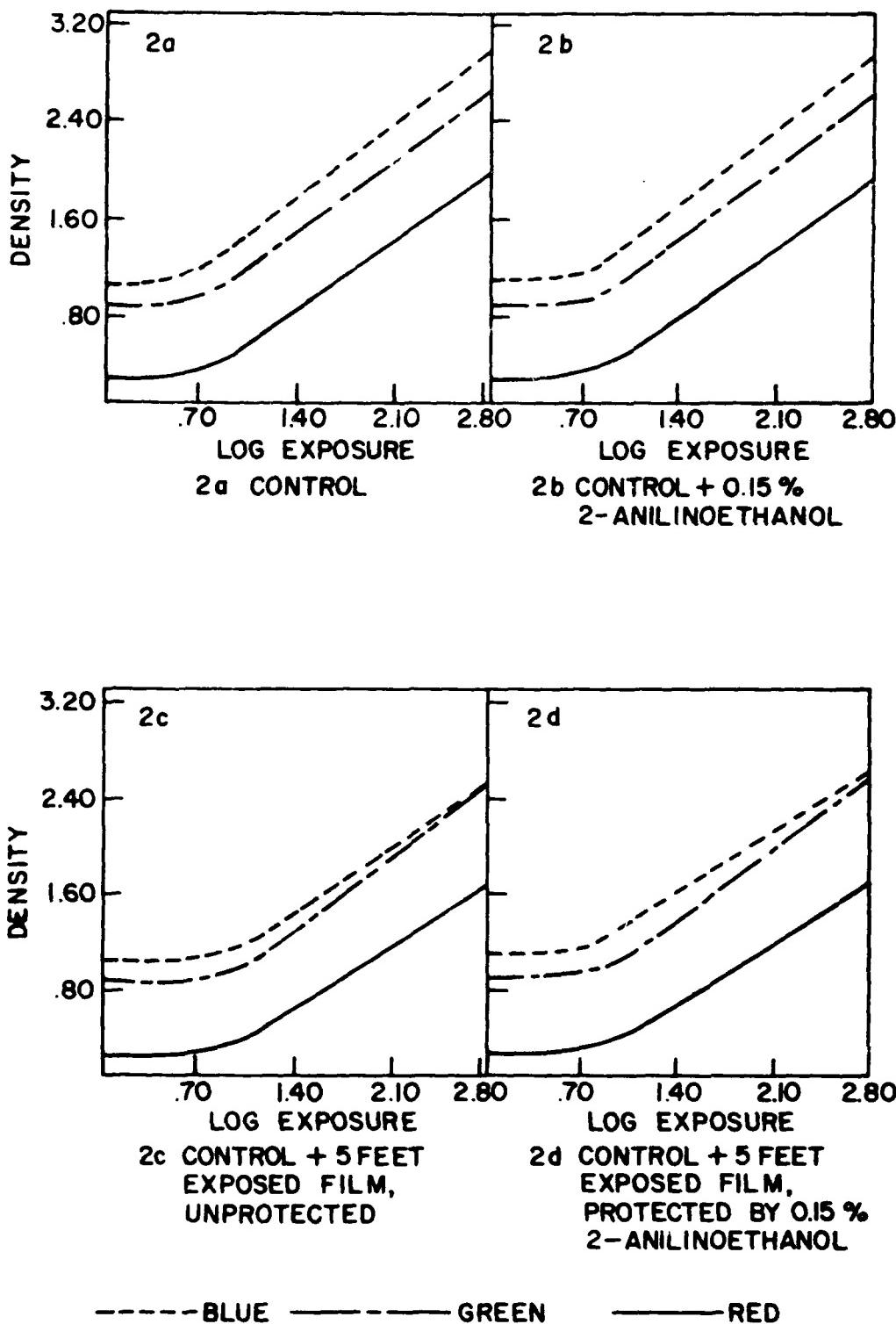


Figure 2. Developer Exhaustion Test. Five feet exposed film in unprotected developer and developer protected by 2-anilinoethanol.

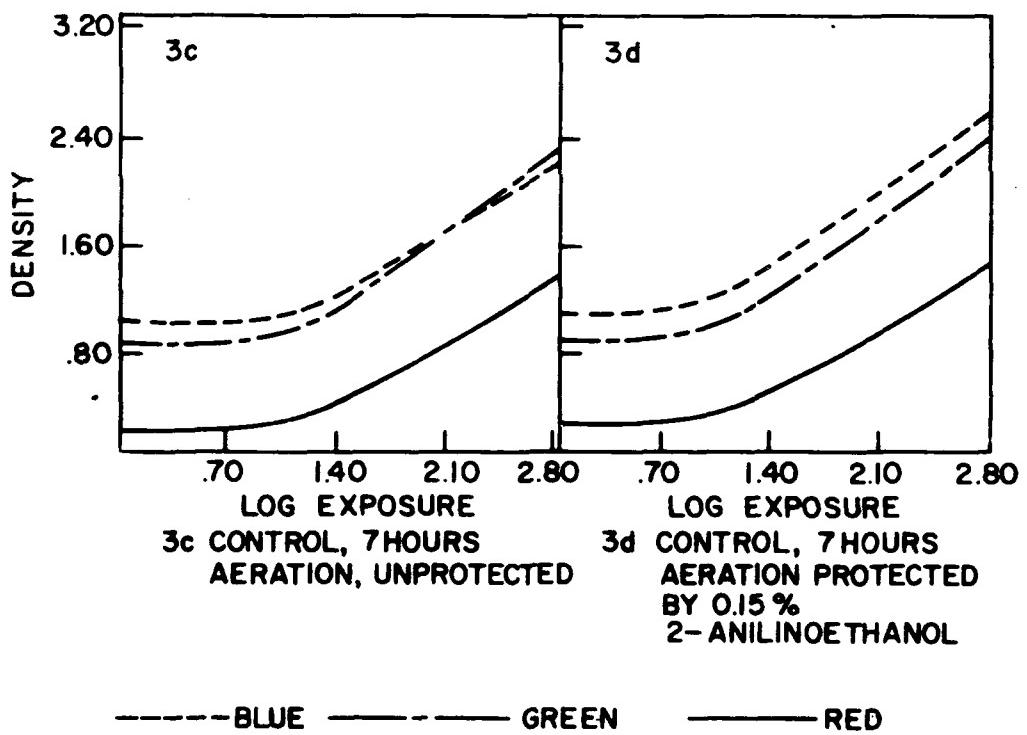
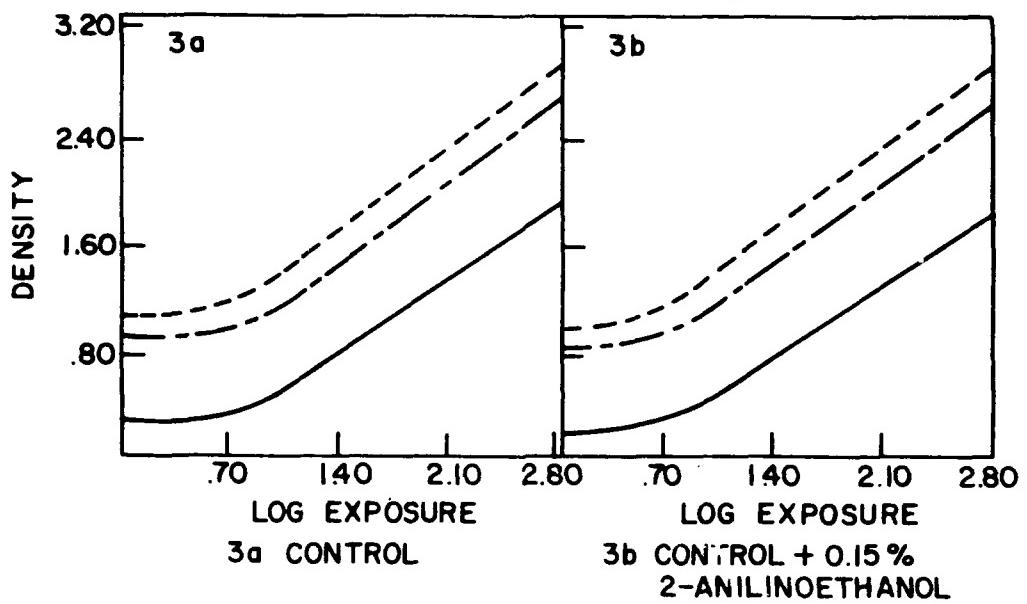
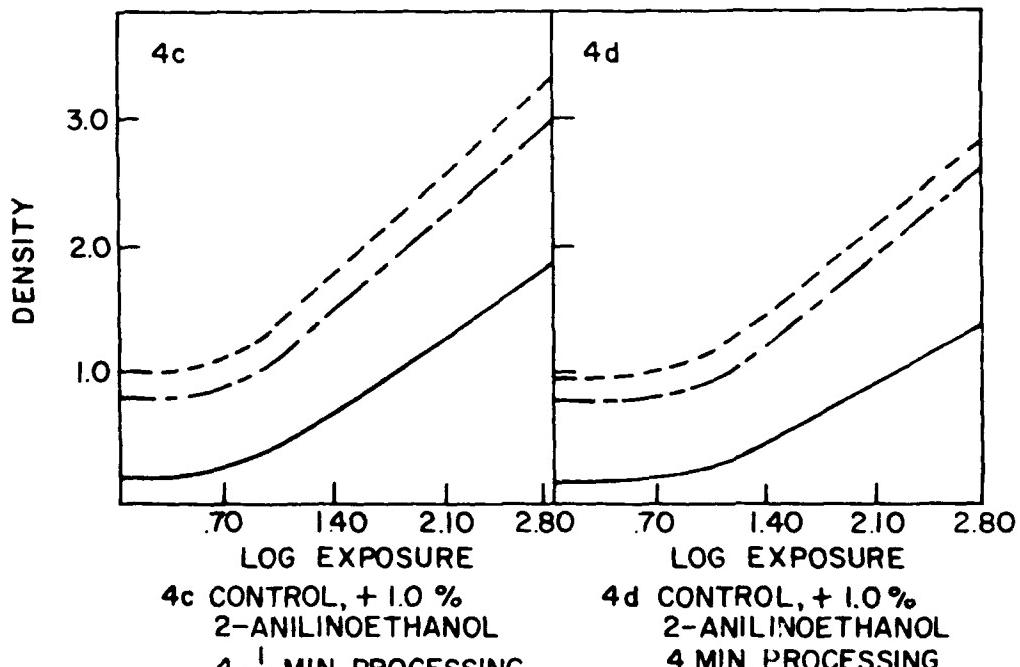
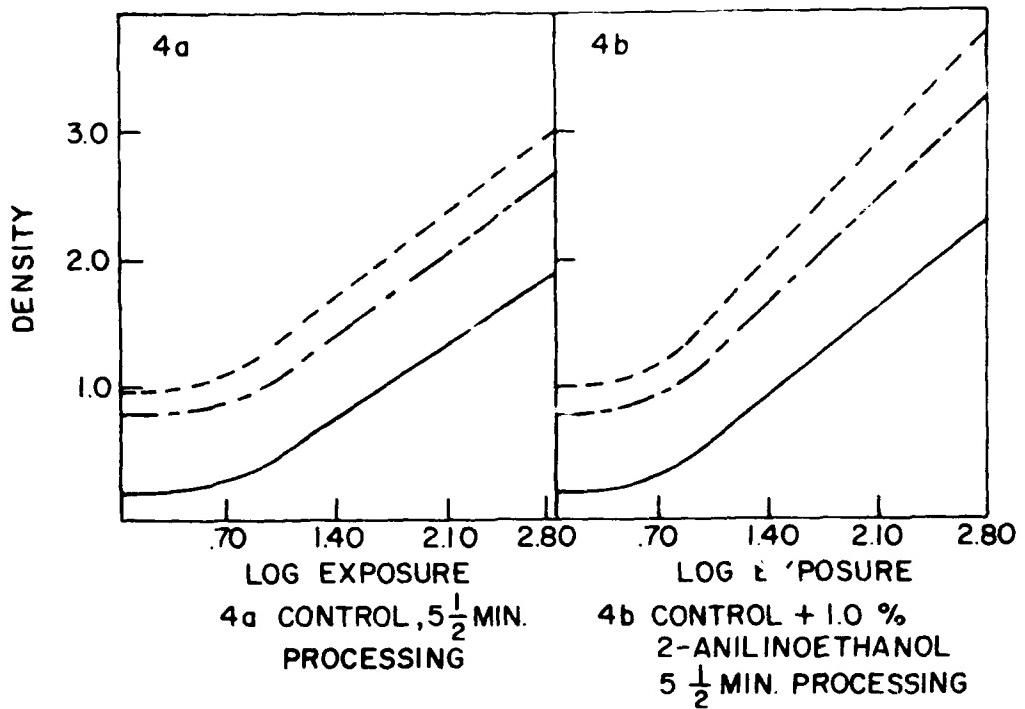


Figure 3. Accelerated Aging Test. Seven hours aeration at rate of 2 liters per minute of unprotected developer and developer protected by 0.15% 2-anilinoethanol.



----- BLUE ----- GREEN ----- RED

Figure 4. Decrease in Development Time on Addition of 1.0% 2-anilinoethanol.

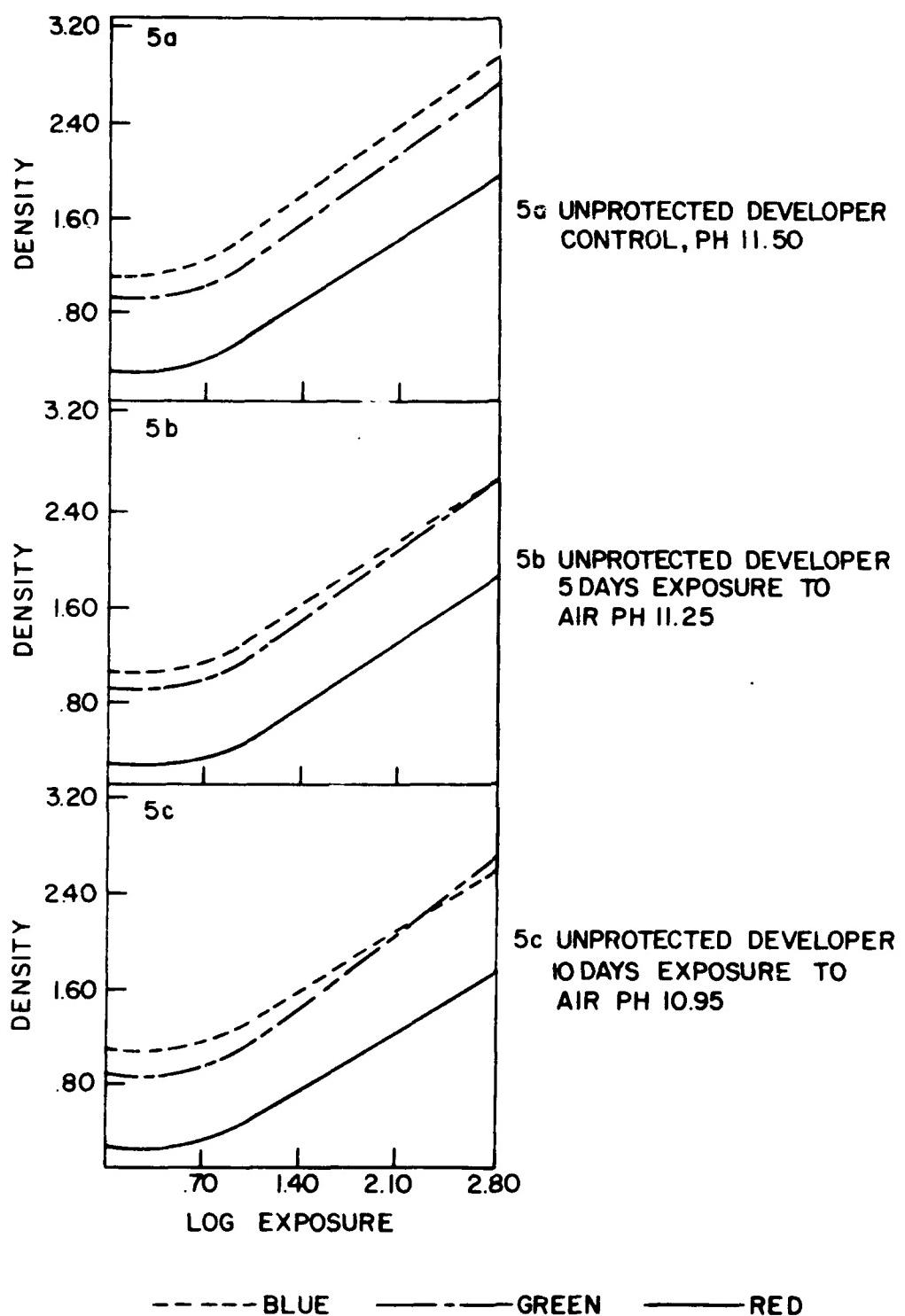


Figure 5. Extended Static Stability Test. Unprotected developer exposed to air for 5 and 10-day periods.

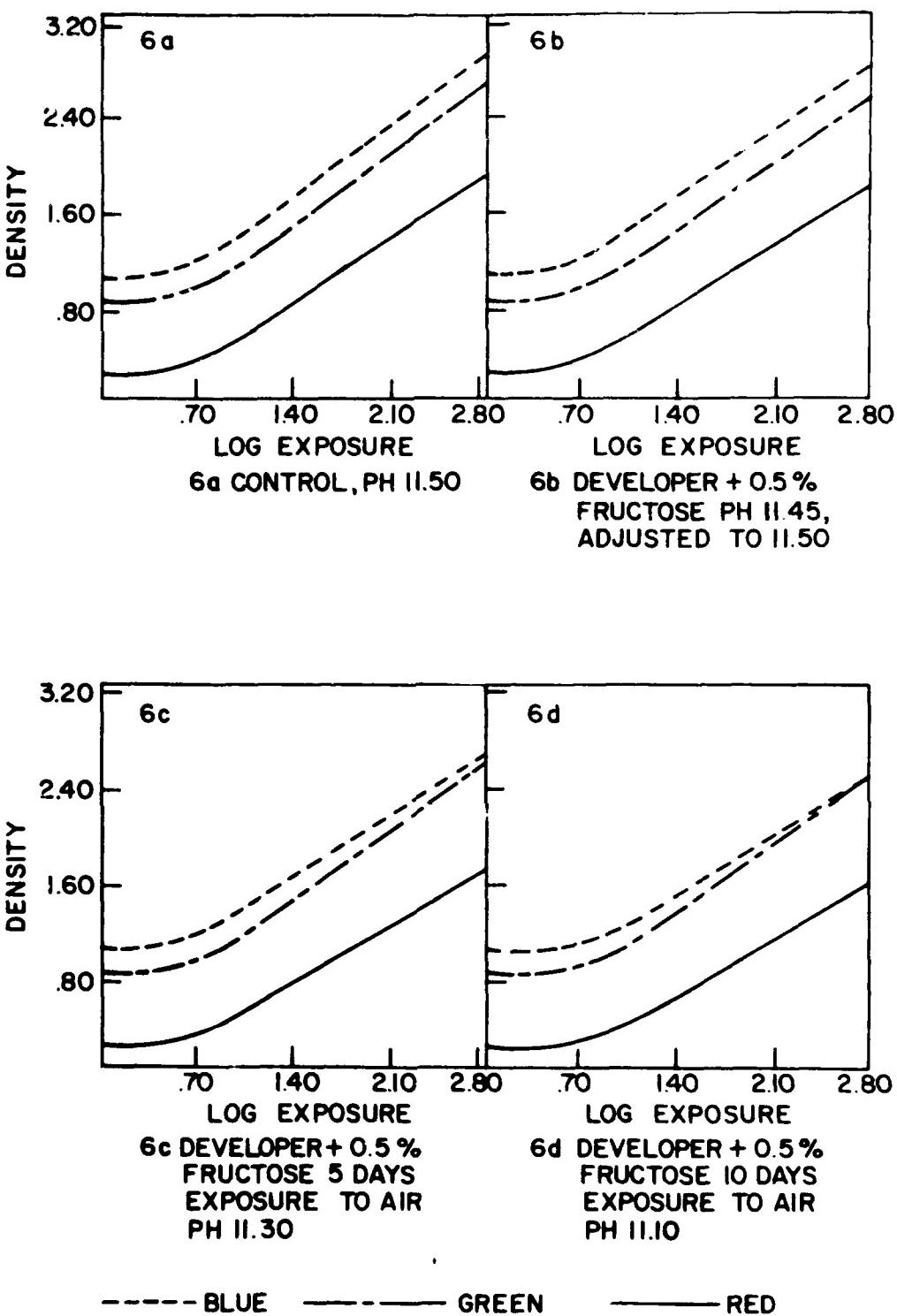


Figure 6. Extended Stability Test. Developer protected by 0.5% fructose, exposed to air for 5 and 10-day periods.

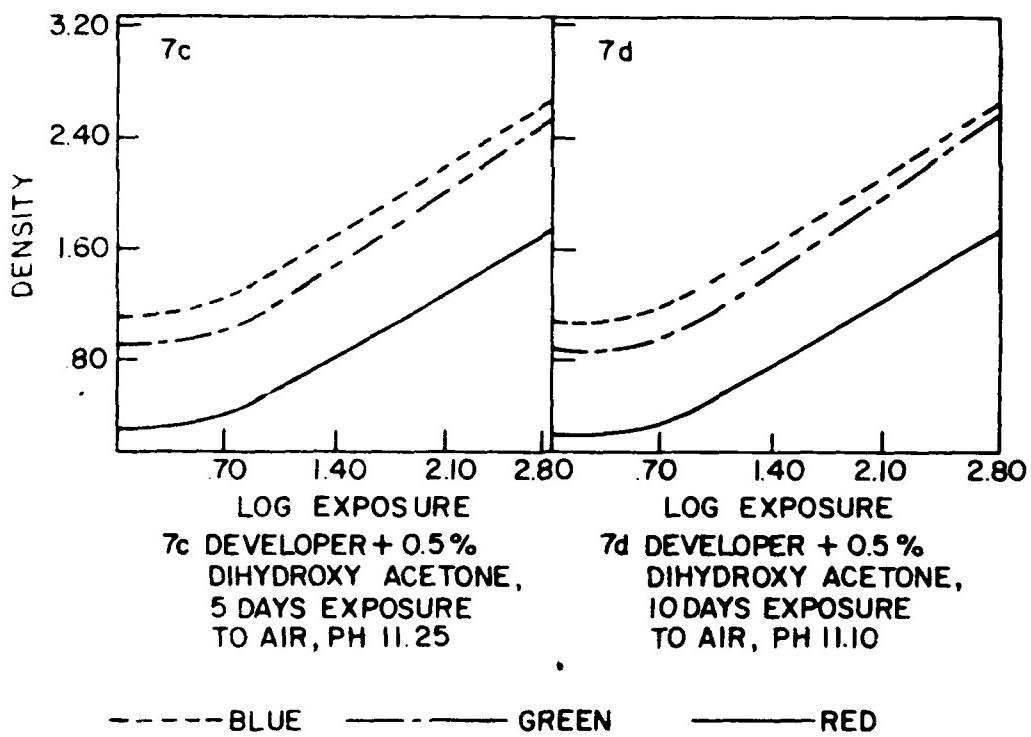
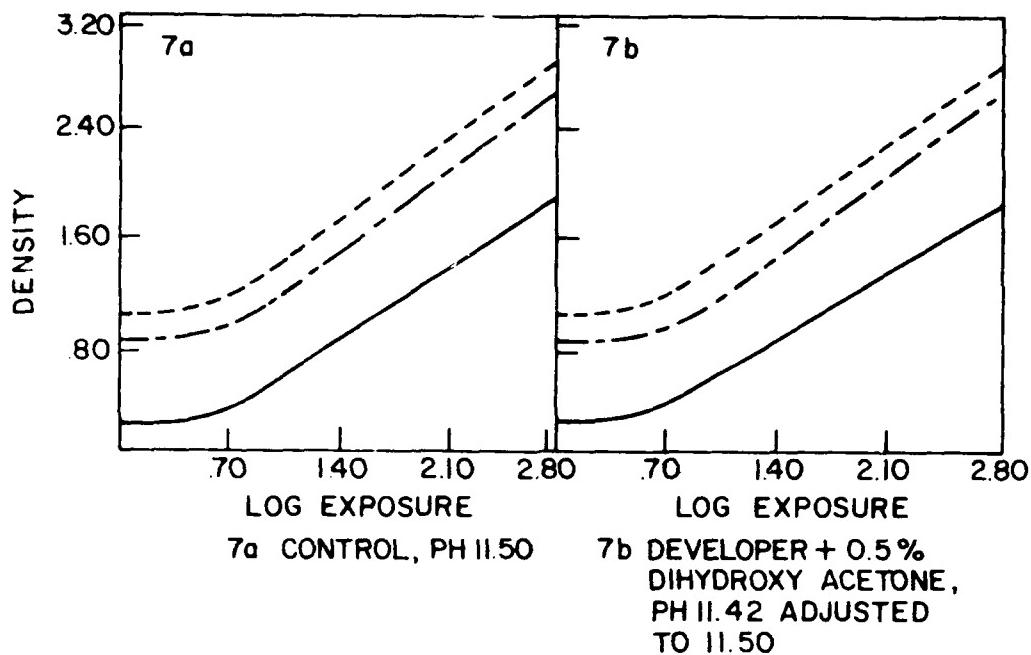


Figure 7. Extended Stability Test. Developer protected by 0.5% di-hydroxy acetone, exposed to air for 5 and 10-day periods.

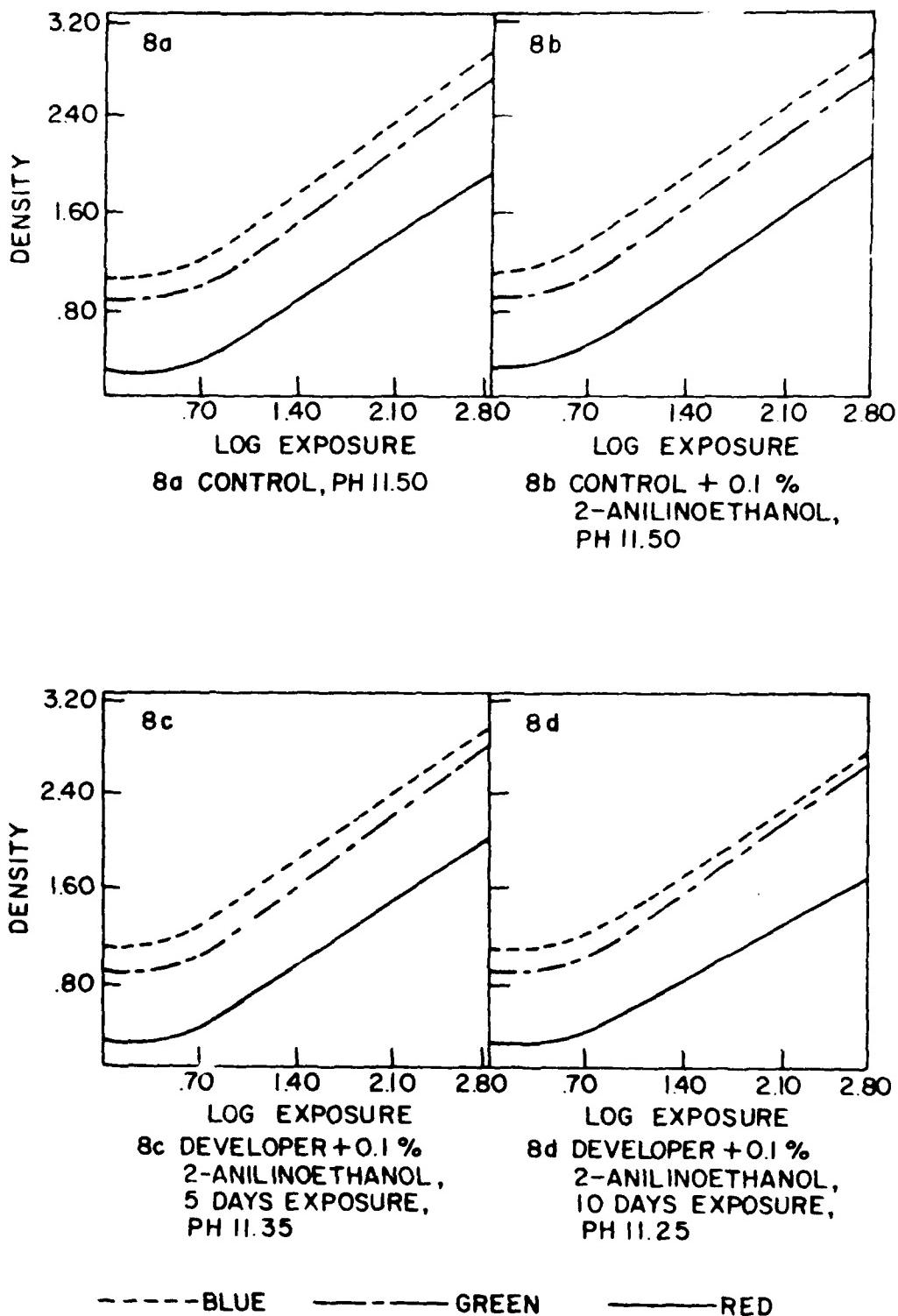


Figure 8. Extended Stability Test. Developer protected by 0.1% 2-anilinoethanol, exposed to air for 5 and 10-day periods.